

Photocatalytical Decomposition of Contaminants on Thin Film Gas Sensors

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Gas sensing materials have been prepared in a form of TiO₂-SnO₂ thin films by rf reactive sputtering from Ti:SnO₂ and Sn:TiO₂ targets. Material studies have been performed by scanning electron microscopy, atomic force microscopy, X-ray diffraction at grazing incidence, Mössbauer spectroscopy, X-ray photoelectron spectroscopy and optical spectrophotometry. Dynamic gas sensing responses have been recorded as reproducible changes in the electrical resistance upon introduction of hydrogen at a partial pressure of 100–6000 ppm over a wide temperature range 473–873 K. Contamination experiments have been carried out with the motor oil (40 vol.% solution in CCl₄) in order to study the effect of UV light illumination on the gas sensor response. Optical spectroscopy has been applied to monitor the photodecomposition of the test compound, bromothymol blue. The Electronic Nose, ALPHA MOS FOX 4000 has been used in order to differentiate between different groups of motor oil vapors.

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1. Introduction

The increasing level of pollution created by our civilization is recognized as the most important issue which has to be addressed in order to prevent further degradation of the environment. There are two distinct approaches to this problem. One requires continuous development of gas sensing methods and devices with a special emphasis on microsystems in air monitoring. An alternative approach is based on the search for new photoactive materials capable to degrade photocatalytically the widest possible range of organic pollutants in air and water. Some oxides, such as SnO₂ and TiO₂ or their mixture SnO₂-TiO₂, are able to serve simultaneously both purposes because they perform well as resistive-type gas sensors [1–4] and photocatalysts assisting in decomposition of organic contaminants [5–9].

The mode of operation of resistive-type gas sensors is based on phenomena of gas–solid interaction that occur at the surface or in the bulk of some metal oxides. A reversible change in the electrical resistance R of the sensing material upon this interaction is considered as a sensor response.

However, the response of resistive-type gas sensors is usually seriously degraded as a result of contamination of their surfaces with organic compounds such as volatile organic compounds (VOCs), carbon soot, oil vapors, etc. This problem is inherently related to the conditions under

which the sensors operate and is especially important for environmental sensors monitoring the atmosphere and its pollution. Sensors working under these conditions suffer from unpredictable, spurious readings and finally they may fail to respond to the external stimulus.

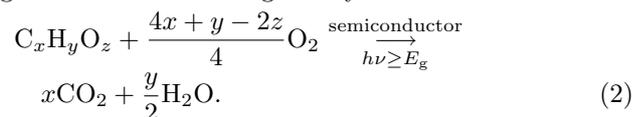
Following the idea proposed by Mor et al. [6] we have undertaken the studies on self-cleaning sensors. The sensors, initially contaminated with a motor oil, are able to retrieve their responses in consequence of the photocatalytic decomposition of contaminants.

Photocatalysis, in the first step, requires generation of electrons e' and holes h' upon absorption of photons with energy $h\nu$ higher than or equal to the energy E_g of the forbidden band gap of the photocatalytic material ($h\nu \geq E_g$). These charge carriers, separately, can participate in redox reactions that result in highly reactive surface ions, suitable for mineralization of organic compounds [5]. The following reaction, in which electrons e' participate:



is an example of reduction of molecular oxygen O₂ to a highly reactive surface ion O₂^{−*}.

The overall mineralization reaction that breaks down organic contaminants is given by



Photoassisted oxidation of the organic contaminant C_xH_yO_z results in its decomposition to CO₂ and H₂O. The band gap energy E_g of the photocatalyst

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should be well-matched to the energy $h\nu$ of the incident photon. The materials presented in this work, TiO_2 and SnO_2 , work as photocatalysts over the UV range of the electromagnetic spectrum.

In this paper we address the issue of the effect of light interaction with the surface of clean and intentionally oil-contaminated resistive-type gas sensors. Evidence of the photodegradation of motor oil in the presence of a photocatalyst has been supported by the optical measurements and multi-sensor analysis of volatile compounds performed with an array of 18 metal oxide sensors so called the electronic nose.

Direct monitoring of the progress in the photodecomposition has been performed previously [9] by means of detection of CO_2 produced according to the reaction (2).

The ultimate aim of our studies is to develop a gas sensor activated by light that could possess the capacity to self-clean and would operate at lower temperatures providing a lower power consumption.

2. Experimental

Gas sensing materials were prepared in a form of TiO_2 - SnO_2 thin films by rf reactive sputtering from $\text{Ti}:\text{SnO}_2$ and $\text{Sn}:\text{TiO}_2$ targets. In order to cover a full compositional range of TiO_2 - SnO_2 mixed oxide system, from 100% of TiO_2 to 100% SnO_2 , the metallic (Ti or Sn) target coverage with dielectric SnO_2 and TiO_2 tablets was varied [7].

Material characterization was performed by standard methods: scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) at grazing incidence (GID). The Mössbauer spectroscopy and X-ray photoelectron spectroscopy (XPS) were carried out in order to find the oxidation states of tin and titanium. The band gap energy E_g was derived from the transmittance and reflectance spectra recorded with a double beam Perkin Elmer Lambda 19 spectrophotometer over the wavelength range from 220 nm to 2500 nm. The details on the experimental techniques used and the results obtained can be found in [7, 8].

Dynamic gas sensing characteristics were recorded in a system shown in Fig. 1. The system consists of six modules:

1. high-temperature oven containing the sensors,
2. temperature controller that stabilizes the temperature in the sensor chamber and the oven cladding,
3. the multiplexer that allows to switch between the measured signals (voltage drop at the Pt-RhPt thermocouple and two sensor resistances at two different current polarizations),
4. the gas flow system equipped with MKS flowmeters and a controller,
5. Hewlett Packard HP34401 A multimeter connected with
6. the PC computer.

Gas sensor dynamic responses are defined as

$$S = \frac{R - R_0}{R_0}, \quad (3)$$

where R is the electrical resistance upon gas introduction and R_0 is the electrical resistance in the reference gas (air). The responses to a reducing gas H_2 were detected over a wide temperature range 473–873 K and hydrogen partial pressure 100–6000 ppm. Hydrogen was mixed with air by adjusting the corresponding flow rates. The total flow was kept constant at 60 sccm. Experiments with the motor oil (40 vol.% solution in CCl_4) contaminated gas sensors were performed as follows. Prior to all experiments, a thin layer of motor oil has been spread over the sensor surface. The sensor characteristics after photocatalytic decomposition of contaminants upon UV illumination were studied *in situ* in the setup shown in Fig. 1. Mercury 500 W lamp was used for UV irradiation.

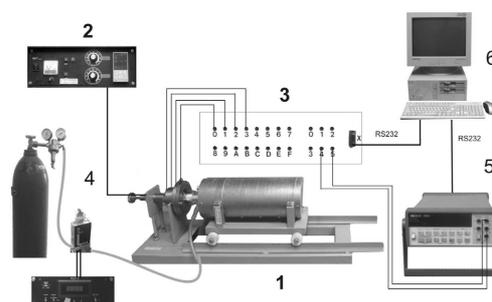


Fig. 1. Experimental setup for gas sensing measurements: 1 — high-temperature sensor chamber, 2 — temperature controller, 3 — multiplexer, 4 — gas flow system, 5 — HP34401A multimeter, 6 — PC.

Decomposition of bromothymol blue (BTB), a typical test compound in the photocatalysis, has been monitored by Perkin Elmer spectrophotometer. The progress in decomposition could be followed indirectly by recording the changes in the optical absorption.

Vapor analysis of pure and photodegraded oil with and without a catalyst was carried out by means of ALPHA MOS model FOX 4000. This electronic nose consists of three chambers housing 6 metal oxide sensors each. The oil samples of 1 mL were heated at 313 K for 5 min in 10 mL sealed glass vials. The headspace of the oil (0.5 mL) was sampled manually, directly into the FOX system. The system acquisition time was 120 s and a flow rate of 150 mL/min of air. A delay of 780 s for purging was used between two consecutive acquisitions to allow sensors to recover.

3. Results and discussion

The summary of TiO_2 - SnO_2 thin films characterization over full compositional range from $x = 0$ to $x = 1$ ($x = \text{Ti}/(\text{Ti} + \text{Sn})$) is given in Table. Apart from TiO_2 ($x = 1$) that crystallizes in the anatase form, all other compositions correspond to rutile. The systematic shift in the angular positions of diffraction peaks can be accounted for by the systematic increase in the interplanar

spacing d_{hkl} with the decreasing x . In Table we have shown the systematic variation of d_{211} from the value typical to TiO_2 anatase at $x = 1$ to that characteristic

for SnO_2 rutile–cassiterite at $x = 0$. This suggests that solid solutions between TiO_2 and SnO_2 are formed within full compositional range $0 < x < 1$.

TABLE

Recapitulation of results from the XRD, XPS and optical spectrophotometry concerning characterization of thin films of TiO_2 – SnO_2 prepared by rf sputtering.

Atomic composition $x = \text{Ti}/(\text{Ti} + \text{Sn})$	Phase composition from XRD	Interplanar spacing d_{211} [nm] from XRD	Binding energy [eV] from XPS	Binding energy shifts [eV] $E_{\text{Sn}3d5/2}$ – $E_{\text{Ti}2p3/2}$	Band gap $E_g \pm 0.01$ [eV] from optical spectrophotometry
1	anatase TiO_2	1.684	$\text{Ti}_{2p3/2} = 458.6$		3.33
0.90	solid state solutions: rutile TiO_2 – SnO_2	1.695		27.6	3.38
0.72		1.715		27.7	3.40
0.53		1.719		27.8	3.50
0.05		1.760		27.8	3.73
0	rutile–cassiterite SnO_2	1.766	$\text{Sn}_{3p5/2} = 486.4$		3.77

Binding energies derived from XPS studies indicate that titanium is present as Ti^{4+} . Mössbauer spectroscopy gave evidence of Sn^{4+} [7]. No changes in the binding energies are imposed by the variation of the film atomic composition x .

Band gap energy E_g increases systematically from that of TiO_2 (3.0 eV for rutile, 3.2 eV for anatase) to that of SnO_2 (3.6 eV) with the decreasing x . The values larger than those expected for well-crystallized samples are due to the substantial contribution from the amorphous phase in thin films.

Figure 2 shows a typical dynamic response of the resistive-type metal oxide gas sensor upon the introduction of a reducing gas. Thin film SnO_2 sensor was exposed to step changes in hydrogen concentration from 200 to 600 ppm H_2 at a constant temperature of 473 K prior to all experiments with contamination. At this relatively low temperature the interaction between a detected gas and the sensor is limited to the surface.

The electrical resistance of SnO_2 and SnO_2 -rich sensors decreases upon interaction with a reducing gas indicating an n -type conductivity of the sensor material. The changes in the electrical resistance are large and reproducible.

Figure 3 shows the absolute value of the sensor response $|S|$ to 1000 ppm of H_2 over the full compositional range for polycrystalline (bulk) and thin film TiO_2 – SnO_2 gas sensors. The absolute value is given because for pure TiO_2 the response to the reducing gases over this temper-

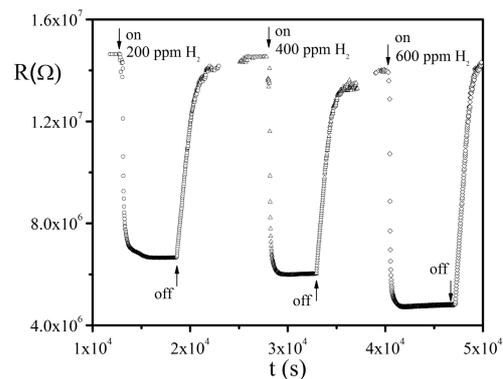


Fig. 2. Dynamic changes of the electrical resistance R upon interaction with hydrogen at 473 K for SnO_2 thin film gas sensor before contamination.

ature range is positive (TiO_2 behaves as a p -type semiconductor) while for all other compositions S is negative. This indicates that incorporation of Sn induces n -type conductivity. As it can be seen in Fig. 3, the optimum operational temperature of the sensor differs significantly over the full compositional range of TiO_2 – SnO_2 . This is a consequence of different mechanisms of gas sensing for TiO_2 and SnO_2 . In the case of TiO_2 , interaction occurs between the gas species and the bulk of the material and is governed by defect equilibria that require higher temperatures of operation [2, 3]. Tin dioxide is a typ-

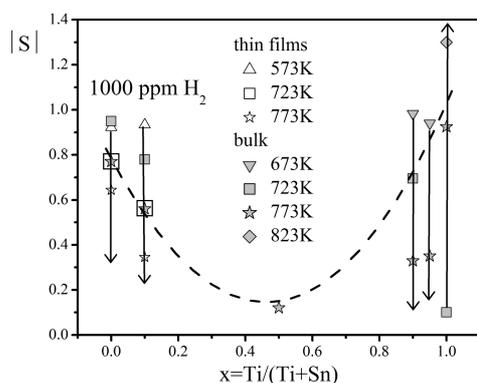


Fig. 3. The absolute value of the sensor response $|S|$ as a function of chemical composition of $\text{TiO}_2\text{-SnO}_2$, $x = \text{Ti}/(\text{Ti} + \text{Sn})$ at different sensing temperatures.

ical surface sensor that can work at lower temperature 570–620 K.

Both TiO_2 -rich compositions (x close to 1) and SnO_2 -rich compositions (x close to 0) yield very good responses at about 573–673 K (Fig. 3). Slightly higher (823 K) operational temperatures are necessary in the case of TiO_2 . Over the intermediate range of compositions ($x = 0.5$) the response S is relatively low even at the elevated temperatures (723 K) which is due to a substantial decrease in the electrical conductivity of the sensing material as indicated by our earlier studies [2]. There is a correlation between the electrical conductivity dependence on x and the gas sensor response.

The effect of motor-oil contamination and subsequent photodegradation as a result of UV irradiation on the sensor response is demonstrated in Fig. 4. The responses of the sensor to a step-change in the hydrogen concentration from 0 to 500 ppm H_2 at a constant temperature of 473 K are compared before surface contamination, after contamination and after irradiation. The sensor reaction to reducing gases is almost completely blocked as a result of the surface contamination with motor oil. Illumination with UV light leads to a partial recovery of the sensor signal.

In order to prove that light assisted decomposition of organic contaminants really takes place on the surface of $\text{TiO}_2\text{-SnO}_2$ thin films, we have performed the optical spectroscopy studies of the test compound — BTB. The absorption spectra of a $\text{TiO}_2\text{-SnO}_2$ thin film with $x = \text{Ti}/(\text{Ti} + \text{Sn}) = 0.92$ before and after it was overcoated with a thin layer of BTB are shown in Fig. 5. Bromothymol blue in acid solution absorbs light over the wavelength range of 400–500 nm. Its absorption band is centered at 440 nm. When the contaminated surface of the $\text{TiO}_2\text{-SnO}_2$ thin film is exposed to UV light for a certain amount of time, the optical absorption decreases over the range of 400–500 nm suggesting the photocatalytic degradation of BTB on the film surface by the UV light. It has been established before these experiments that such an effect does not take place without a $\text{TiO}_2\text{-}$

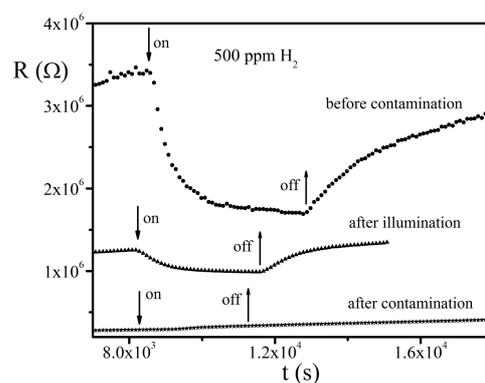


Fig. 4. The effect of motor-oil contamination and its photodegradation by UV light on the sensor response, i.e., electrical resistance R of SnO_2 thin film sensor to a step-change in the hydrogen concentration from 0 to 500 ppm at a constant temperature of 473 K.

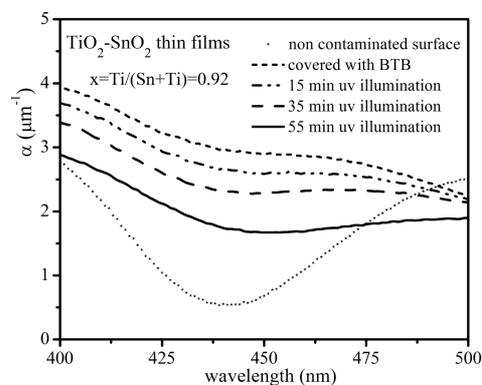
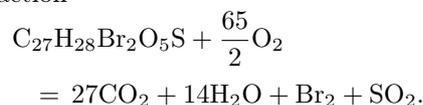


Fig. 5. The influence of the UV illumination time on the optical absorption spectrum α of $\text{TiO}_2\text{-SnO}_2$ thin film covered with a layer of bromothymol blue; the spectra of uncovered $\text{TiO}_2\text{-SnO}_2$ thin film and that of the film covered with bromothymol blue prior to the illumination are included as references.

SnO_2 catalyst. Successive experiments with the increasing irradiation time result in a systematic decrease in the optical absorption. The oxidation of bromothymol blue to CO_2 and H_2O is activated by UV light at the surface of $\text{TiO}_2\text{-SnO}_2$ thin film according to the mineralization reaction



In order to make sure that the UV irradiation results in the photo-assisted rather than thermal decomposition of oil, the experiments were performed at room temperature with a constant monitoring of both temperature and electrical resistance of the sensor. The results are included in Fig. 6.

The influence of UV illumination upon the sensor response manifests itself as a progressive decrease in the electrical resistance of the sensor as a function of the

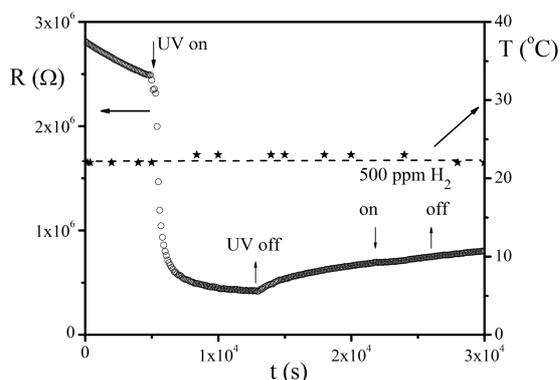


Fig. 6. Dynamic changes in the electrical resistance R of motor-oil contaminated SnO_2 thin film sensor upon UV irradiation. The experiment was performed at room temperature.

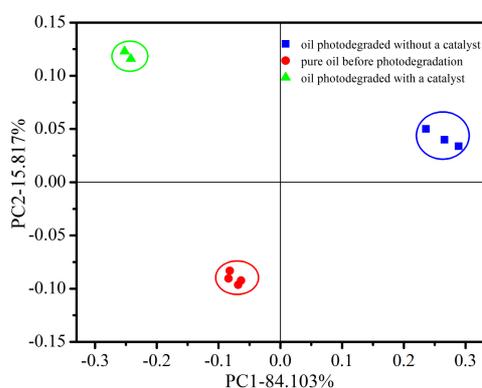


Fig. 7. PCA of the results of the experiments performed with Alpha MOS on vapors of pure and photodegraded motor oil.

irradiation time. This effect is a result of the increased concentration of charge carriers because of the photogeneration of electron-hole pairs. The temperature remains unaffected by UV illumination as seen in Fig. 6.

After switching the UV light off, the electrical resistance increases, but does not reach the level before UV illumination, i.e., the process is irreversible. The irreversible changes in the electrical resistance are due to the surface decomposition of the motor oil assisted by the UV light.

No significant changes in the temperature recorded (Fig. 6) confirm that the electronic effect predominates over thermal effects. Our earlier studies indicated that the thermal decomposition of this type of oil becomes significant at around 300 °C.

Following the method described in [10], we have applied an array of gas sensors, Electronic Nose Alpha MOS 4000 in order to discriminate between the vapors of pure oil, photodegraded oil without and with the photocatalysts TiO_2 . Figure 7 demonstrates the results of the prin-

cipal components analysis (PCA). The PCA constructs linear combinations of the original data from the 18 resistive type metal oxide sensors with maximum variance. This reduces the number of variables represented by 18 sensors responses to a smaller number of components with minimal loss of information. The first component PC1 accounts for the greatest change in variance. The second component PC2 represents the second largest contribution to the variance.

As shown in Fig. 7 we could differentiate by PCA between three groups. The pure oil, the photodegraded without the photocatalysts, and that degraded by light in the presence of a photocatalyst TiO_2 clearly belong to different groups.

4. Conclusions

TiO_2 - SnO_2 mixed oxide materials over full compositional range $x = \text{Ti}/(\text{Ti} + \text{Sn})$ varied between $x = 0$ (SnO_2) and $x = 1$ (TiO_2) were obtained in the form of rf-sputtered thin films. The best response of TiO_2 - SnO_2 sensors to hydrogen was obtained for SnO_2 -rich and TiO_2 -rich compositions and was found to be correlated with the electrical conductivity dependence upon x .

Experiments with the motor oil contaminated and UV irradiated TiO_2 - SnO_2 thin film sensors indicated the photodegradation of organic contaminants at the surface. Partial recovery of the sensor response to hydrogen has been demonstrated. From the point of view of the ultimate aim of this work, the TiO_2 - SnO_2 mixed oxide system offers much promise as a sensitive sensor in which the function of self-cleaning by light activation over the UV range could be implemented.

Acknowledgments

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